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Ferroelectric Liquid Crystals Induced by Atropisomeric Biphenyl Dopants: Correlation between the Sign of Induced Polarization and the Absolute Configuration

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A new synthetic route to a known series of five chiral dopants with atropisomeric biphenyl cores was developed which enabled the assignment of their absolute configurations. These compounds can be doped in achiral SmC liquid crystal hosts to give ferroelectric SmC* liquid crystals with a spontaneous polarization P_S that scales with the dopant concentration. One of these dopants, (*R*)-2,2′,6,6′-tetramethyl-3,3′-dinitro-4,4′-bis[(4-nonyloxybenzoyl)oxy]biphenyl ((*R*)-**1**), exhibits one of the highest polarization powers ever reported. The atropisomeric cores were obtained in optically pure form via the resolution of bis-(1*S*)-10-camphorsulfonamido diastereomers, which were then hydrolyzed to the corresponding diaminobiphenyl enantiomers (X = NH_2), and converted to the substituted biphenyl cores (X = NO_2, F, Cl, Br, Me) using standard functional group interconversion methods. The absolute configurations of the five chiral dopants were assigned based on the X-ray crystallographic analysis of the diastereomer (*R*)-3,3′-bis[(1*S*)-10-camphorsulfonamido]-2,2′,6,6′-tetramethyl-4,4′-dimethoxybiphenyl, and correlated to the sign of spontaneous polarization each dopant induces in the achiral SmC host 2-(4-butyloxyphenyl)-5-octyloxypyrimidine (**PhP1**).

Introduction

Over the past two decades, the development of chiral smectic liquid crystals, including ferroelectric SmC*, antiferroelectric SmC_a* and electroclinic SmA* phases, has led to major advances in electrooptical spatial light modulator technologies.[1] Already, color viewfinders based on high-resolution reflective FLC microdisplay technology can be found in commercial products such as digital cameras and camcorders.[2,3] In a surface-stabilized planar alignment, SmC* liquid crystals exhibit a spontaneous polarization P_S that coincides with the polar C_2 symmetry axis of the SmC* phase (Figure 1).[4] This polarization can be coupled to an electric field to produce a bistable electrooptical light shutter with a switching time on the order of μs.[5] The performance characteristics of FLC displays depend in part on the magnitude of P_S, and significant research efforts have focused on understanding the relationship between the molecular structure of the chiral constituent(s) of a SmC* material and the magnitude of P_S.[6−8] In commercial FLC formulations, the spontaneous polarization is induced by mixing small amounts of a chiral dopant with high polarization power (δ_p) into an achiral SmC mixture with low viscosity and wide temperature range.[9]

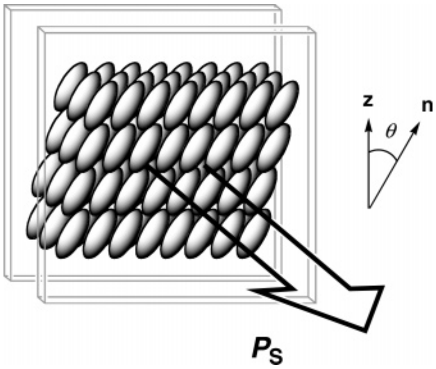

Figure 1. Schematic representation of the chiral SmC* phase as a surface-stabilized FLC film between two glass slides. The layer normal **z** and the time-average orientation of molecular long axes (director) **n** are in the plane of the page and form a tilt angle θ. The spontaneous polarization P_s is coincident with the C_2 symmetry axis of the FLC and is normal to the plane of the page. The sign of P_S is negative according to the physics convention.[10]

The spontaneous polarization is a macroscopic chiral property, i.e, it is either left-handed (negative) or right-handed (positive) depending on the absolute configuration of the chiral dopant. The sign of P_S shown in Figure 1 is negative and conforms to the physics convention which is normally used in the literature to characterize SmC* phases.[10] At the microscopic level, the spontaneous polarization originates from a preference of transverse molecular dipoles to orient in one direction along

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(1) (a) Lagerwall, S. T. *Ferroelectric and Antiferroelectric Liquid Crystals*; Wiley-VCH: Weinheim, 1999. (b) Clark, N. A.; Lagerwall, S. T. In *Ferroelectric Liquid Crystals: Principles, Properties and Applications*; Goodby, J. W.; Blinc, R.; Clark, N. A.; Lagerwall, S. T.; Osipov, M. A.; Pikin, S. A.; Sakurai, T.; Yoshino, K.; Zeks, B., Eds.; Gordon and Breach: Philadelphia, PA, 1991; pp 409−452. (c) Dijon, J. In *Liquid Crystals: Applications and Uses*; Bahadur, B., Ed.; World Scientific: Singapore, 1990; Vol. 1, Chapter 13.

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(3) Walba, D. M. *Science* **1995**, *270*, 250.

(4) Meyer, R. B.; Liebert, L.; Strzelecki, L.; Keller, P. *J. Phys. (Paris) Lett.* **1975**, *36*, L69.

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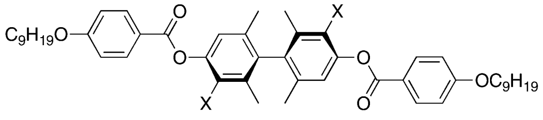
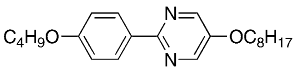
10.1021/cm0489845 CCC: $27.50

the polar C_2 axis of the SmC* phase due to an asymmetry in the conformational energy profile of any polar functional group sterically coupled to a stereogenic center. Empirical and semiempirical structure−property relationships based on conformational analyses of such stereo-polar units are well established for dopants with chiral side-chains, and are generally accurate in predicting the sign of P_S for a given absolute configuration.[6,7,11,12] The polarization power of such compounds is normally invariant with respect to the structure of the SmC host, which is consistent with the Boulder model for the molecular origins of P_S.[13] According to this model, the SmC phase is considered to be a supramolecular host, and the conformational and orientational ordering of a chiral dopant is modeled by a mean field potential which qualitatively behaves like a binding site analogous to that described in host−guest chemistry. The binding site is C_{2h} symmetric and has a zigzag shape (vide infra) that is assumed to be invariant with respect to the host structure. As a first approximation, the Boulder model assumes that a chiral dopant plays the role of a "passive" guest which adopts a conformation that best fits the achiral binding site of the SmC host.

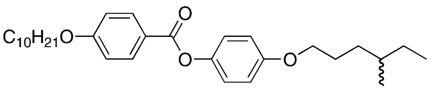
Unlike conventional dopants with chiral side-chains, chiral dopants with atropisomeric biphenyl cores such as **1**−**5** behave as "active" dopants and exhibit polarization powers that vary significantly with the structure of the SmC host.[8] For example, the polarization power of dopant **1** ranges from 1555 nC/cm^2 in the phenylpyrimidine host **PhP1**, one of the highest δ_p values reported thus far, to less than 30 nC/cm^2 in the phenyl benzoate host **PhB**. According to recent probe experiments, this host effect is due, at least in part, to a chiral perturbation propagated via core−core interactions with SmC host molecules.[14] We proposed that this perturbation results in a chiral distortion of the SmC binding site as a feedback effect. Such a chiral distortion may amplify the polarization power of the dopant by causing a shift in the conformational equilibrium of the atropisomeric core favoring one orientation of its transverse dipole moment along the polar axis of the SmC* phase. The chirality transfer feedback (CTF) model may be viewed conceptually as an extension of the original Boulder model that accounts for the effect of chiral perturbations exerted by a dopant on a SmC liquid crystal host.



1, X = NO_2; **2**, X = F; **3**, X = Cl; **4**, X = Br; **5**, X = CH_3



PhP1



PhB

Variations in polarization power as a function of the symmetry-breaking groups X observed with the series **1**−**5** in the host **PhP1** were analyzed in terms of the effect of X on the transverse dipole moment of the core ($\mu_\perp$), on the conformational energy profile for rotation of the core with respect to the side-chains in the SmC binding site, and on the ability of the core to exert a chiral perturbation on the SmC host.[15] The results of this analysis proved to be consistent with the CTF model although we were unable to assign the absolute configurations of the atropisomeric cores. In this paper, we report the absolute configurations of dopants **1**−**5** in relation to the handedness of the spontaneous polarizations they induce in the SmC host **PhP1**.

Results

Synthesis and Determination of Absolute Configuration. The absolute configurations of dopants **1**−**5** were assigned by X-ray crystallographic analysis of the bis-(S)-camphorsulfonamide derivative (S,S,R)-**10**, which was synthesized according to Scheme 1. Homocoupling of the known aryl bromide **6**[16] via oxidation of the corresponding cyanocuprate gave the biphenyl **7**,[17,18] which was nitrated under standard conditions to give **8** in 48% yield. Reduction with stannous chloride gave the racemic diamine **9** in 79% yield, which was then derivatized with (1S)-(+)-10-camphorsulfonyl chloride to give the bis-sulfonamide **10** as a diastereomeric mixture. Separation of the two diastereomers was achieved by repeated recrystallizations from methanol and toluene to give (S,S,R)-**10** and (S,S,S)-**10** in 36% and 42% yields, respectively. Crystals suitable for X-ray

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(7) Goodby, J. W. In *Ferroelectric Liquid Crystals: Principles, Properties and Applications*; Goodby, J. W., Blinc, R., Clark, N. A., Lagerwall, S. T., Osipov, M. A., Pikin, S. A., Sakurai, T., Yoshino, K., Zeks, B., Eds.; Gordon & Breach: Philadelphia, PA, 1991; pp 99−157.

(8) Lemieux, R. P. *Acc. Chem. Res.* **2001**, *34*, 845.

(9) The polarization power measures the propensity of a chiral dopant to induce a spontaneous polarization P_S according to the equation:

$$\delta p = \left(\frac{dP_o(x_d)}{dx_d}\right)_{x_d \to 0}$$

where x_d is the dopant mole fraction and P_o is the reduced polarization of the SmC* phase. Siemensmeyer, K.; Stegemeyer, H. *Chem. Phys. Lett.* **1988**, *148*, 409. The reduced polarization is normalized for variations in tilt angle θ and is equal to $P_S \sin \theta^{-1}$. Kuczynski, W.; Stegemeyer, H. *Chem. Phys. Lett.* **1980**, *70*, 123.

(10) According to the physics convention, the spontaneous polarization points from the negative to the positive end of a dipole, which is opposite to that used in chemistry. A positive polarization vector points in the same direction as to the cross product of the layer normal and the director, $\mathbf{z} \times \mathbf{n}$.[6]

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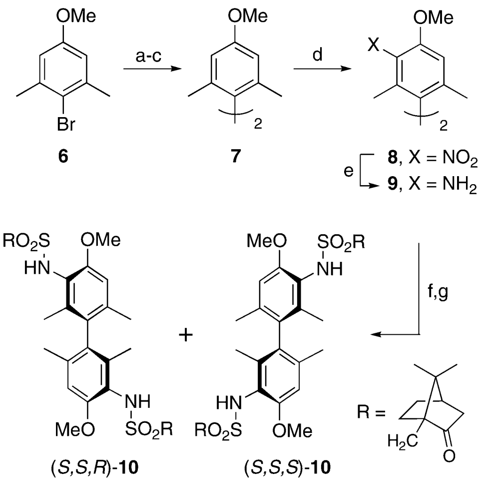
Scheme 1[a]



[a] Reagents and conditions: (a) n-BuLi, THF, −78 °C; (b) CuCN; (c) O_2; (d) HNO_3, H_2SO_4/AcOH, 25 °C; (e) $SnCl_2{\cdot}2H_2O$, EtOH, reflux; (f) (1*S*)-(+)-10-camphorsulfonyl chloride, Et_3N, CH_2Cl_2; (g) recrystallization from MeOH (*S*,*S*,*R*) and toluene (*S*,*S*,*S*).

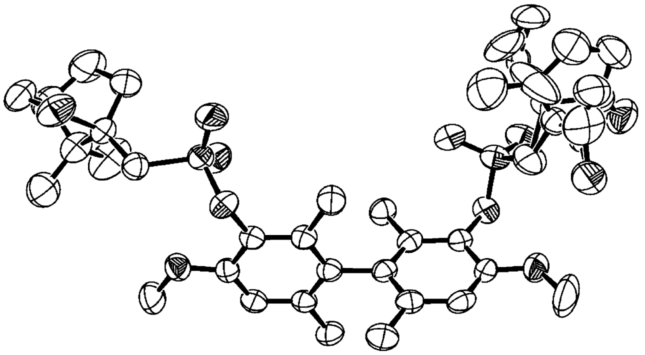
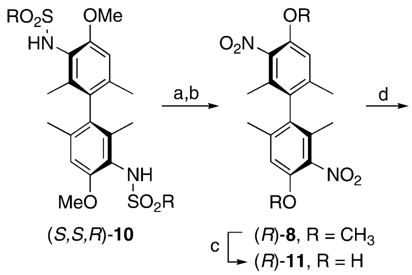


Figure 2. Crystal structure of (*S*,*S*,*R*)-**10**.

diffraction were obtained for the diastereomer recrystallized from methanol, and the resulting crystal structure shown in Figure 2 established the helicity of the atropisomeric core as *M* and the absolute configuration as (*R*).[19]

Dopants of known absolute configurations were derived from either (*S*,*S*,*R*)-**10** or (*S*,*S*,*S*)-**10**, as shown in Schemes 2 and 3. The dinitro dopant (*R*)-**1** was obtained by hydrolysis of (*S*,*S*,*R*)-**10** with concentrated HBr, followed by oxidation of the resulting diamine with mCPBA to give (*R*)-**8** in 18% yield. Cleavage of the methoxy groups with BBr_3 gave the known dinitro diol (*R*)-**11** in 67% yield, which was then esterified using DCC and DMAP to give (*R*)-**1**. The dopants (*S*)-**2**−**5** were derived from (*S*,*S*,*S*)-**10** by hydrolysis to the diamine (*S*)-**9** in 40% yield, followed by conversion to the bis-diazonium salt and treatment with KI to give the diiodo intermediate (*S*)-**12** in 53% yield. The known dichloro and dibromo diols (*S*)-**13** and (*S*)-**14** were obtained in 68−70% yield by treatment of (*S*)-**12** with CuCl and CuBr, respectively, followed by cleavage of the methoxy groups with BBr_3. The known difluoro and dimethyl diols (*S*)-**15** and (*S*)-**16** were obtained from (*S*)-**12** in 63% yield via lithium−halogen exchange and trapping with $(PhSO_2)_2NF$ and MeI, respectively, followed by cleavage of the methoxy groups with BBr_3. Each diol was esterified using DCC and DMAP to give (*S*)-**2**−**5**.

Scheme 2[a]



[a] Reagents and conditions: (a) 48% HBr, AcOH, reflux; (b) mCPBA, $CHCl_3$, 0 °C; (c) BBr_3, CH_2Cl_2, −78 °C; (d) 4-nonyloxybenzoic acid, DCC, DMAP, CH_2Cl_2, 25 °C.

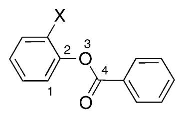
Table 1. Measured and Predicted Signs of Induced Polarization P_S in PhP1

dopant	X	observed sign of P_S	predicted sign of P_S
(*R*)-**1**	NO_2	−	−
(*S*)-**2**	F	+	+
(*S*)-**3**	Cl	+	−
(*S*)-**4**	Br	+	+
(*S*)-**5**	Me	−	−

Sign of Induced Polarization. Compounds (*R*)-**1** and (*S*)-**2**−**5** were doped in the host **PhP1** at a mole fraction of 4 mol %. Well-aligned SSFLC films were obtained by slow cooling of the mixtures from the isotropic liquid to the SmC* phase in rubbed polyimide-coated ITO glass cells with a 4-μm gap. The sign of polarization was determined by polarized optical microscopy at 5 K below the SmA*−SmC* phase transition temperature ($T - T_C = -5$ K) based on the relative configuration of a 9 V dc field and the switching position of the sample according to the physics convention.[10] The results are listed in Table 1.

Discussion

The polar ordering of dopants **1**−**5** within the confines of the SmC binding site is thought to originate from a small asymmetric bias in the energy profile for rotation of the rigid biphenyl core about the two ester C−O bonds, which results in a preferred orientation of the core transverse dipole moment $\mu_\perp$ along the polar axis of the SmC* phase (Figure 3). The effect of the symmetry-breaking group X on the energy profile for rotation about the ester C−O bond was previously modeled by ab initio calculations at the B3LYP/6-31G(d) level on the simplified phenyl benzoate substructure **17**, as shown in Figure 4.[15]



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To predict the sign of P_S induced by (*R*)-**1** and (*S*)-**2**−**5**, the direction of the transverse dipole moment of each dopant with respect to the polar axis was determined based on a reasonable approximation of the lowest energy conformation of the dopant in the SmC host that is consistent with the Boulder model. Hence, we assumed that each dopant adopts a C_2-symmetric zigzag

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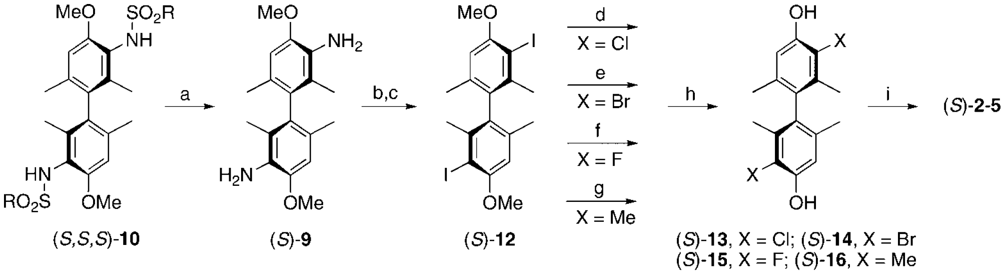
[19] Eliel, E. L.; Wilen, S. H.; Mander, L. N. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994.

Scheme 3^a



^{a} Reagents and conditions: (a) 48% HBr, AcOH, reflux; (b) $NaNO_2$, 10% H_2SO_4, 0 °C; (c) KI, H_2O, reflux; (d) CuCl, DMF, reflux; (e) CuBr, pyridine, reflux; (f) *n*-BuLi, THF, −78 °C, then $(PhSO_2)_2NF$; (g) *n*-BuLi, THF, −78 °C, then MeI; (h) BBr_3, CH_2Cl_2, −78 °C; (i) 4-nonyloxybenzoic acid, DCC, DMAP, CH_2Cl_2.

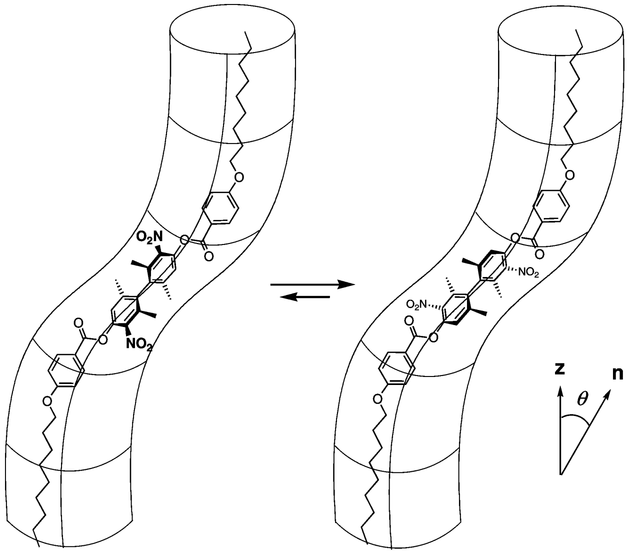


Figure 3. Rotation of the biphenyl core about the two ester C−O single bonds of dopant (*R*)-**1** confined to the binding site of the Boulder model in a C_2-symmetric zigzag conformation. The polar axis is normal to the plane of the page.

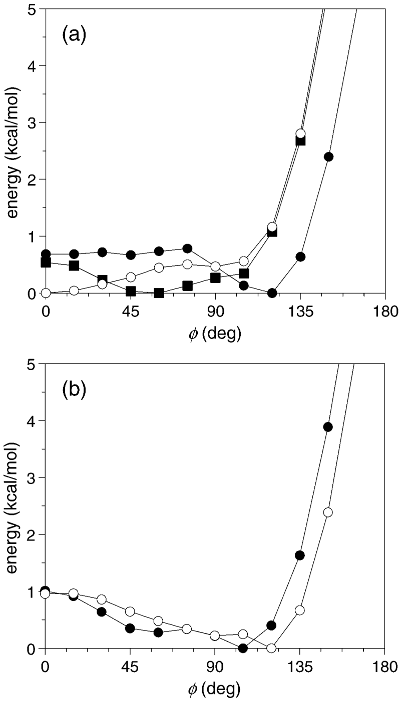


Figure 4. Energy profiles as a function of the dihedral angle ϕ defined by atoms 1, 2, 3, and 4 in the model compound **17** according to B3LYP/6-31G(d) calculations (from ref 15): (a) X = F (●), X = Cl (■), X = Br (○); (b) X=NO_2 (○), X = Me (●).

conformation that conforms to the binding site of the Boulder model, with the core more tilted than the side-chains and the two 4-alkoxybenzoate groups approximately antiparallel to each other. The resulting structures, shown as side-on views in Figure 5, and schematically as end-on views in Figure 6, were minimized at the semiempirical AM1 level with the dihedral angle ϕ formed by the C(O)−O bond and the plane of the phenyl ring fixed at the minimum energy value calculated at the B3LYP/6-31G(d) level. The minimized structures in Figure 5 are oriented relative to a frame of reference in which the polar axis of the SmC* phase is perpendicular to the plane of the page, with the molecular C_2 axes coincident with the polar axis. The direction of the transverse dipole moment calculated at the AM1 level for each structure conforms to the physics convention, i.e., the $\mu_\perp$ vector points from negative to positive.[15] As shown in Table 1, the predicted signs of P_S are in agreement with the experimental data except for the dichloro dopant (*S*)-**3**, which may be explained by the relatively flat rotational energy profile calculated for X = Cl compared to those calculated for the other model systems. Indeed, the calculations for the halogen series suggest that the position of the energy minimum depends on a delicate balance between electronic and steric effects which in the case of X = Cl may be tipped in one direction or the other by packing forces in the condensed phase that cannot be accounted for in gas-phase calculations.

Conclusion

A new synthesis of the atropisomeric biphenyl dopants **1**−**5** enabled the assignment of their absolute configurations by X-ray crystallography. The signs of spontaneous polarization induced by (*R*)-**1** and (*S*)-**2**−**5** in the achiral SmC host **PhP1** were determined by polarized microscopy and correlated to those predicted by the Boulder model. The predicted and experimental signs of P_S are in agreement, except in one case, (*S*)-**3**, which is characterized by a conformational energy minimum in the gas phase that may be more susceptible to perturbations by packing forces in the condensed phase than the other dopants. The chloro-substituted dopant (*S*)-**3** notwithstanding, the agreement between the predicted and experimental signs of P_S suggests that our description of the polar ordering of these dopants in the SmC host **PhP1** according to the Boulder model is valid. Furthermore, these results are consistent with the

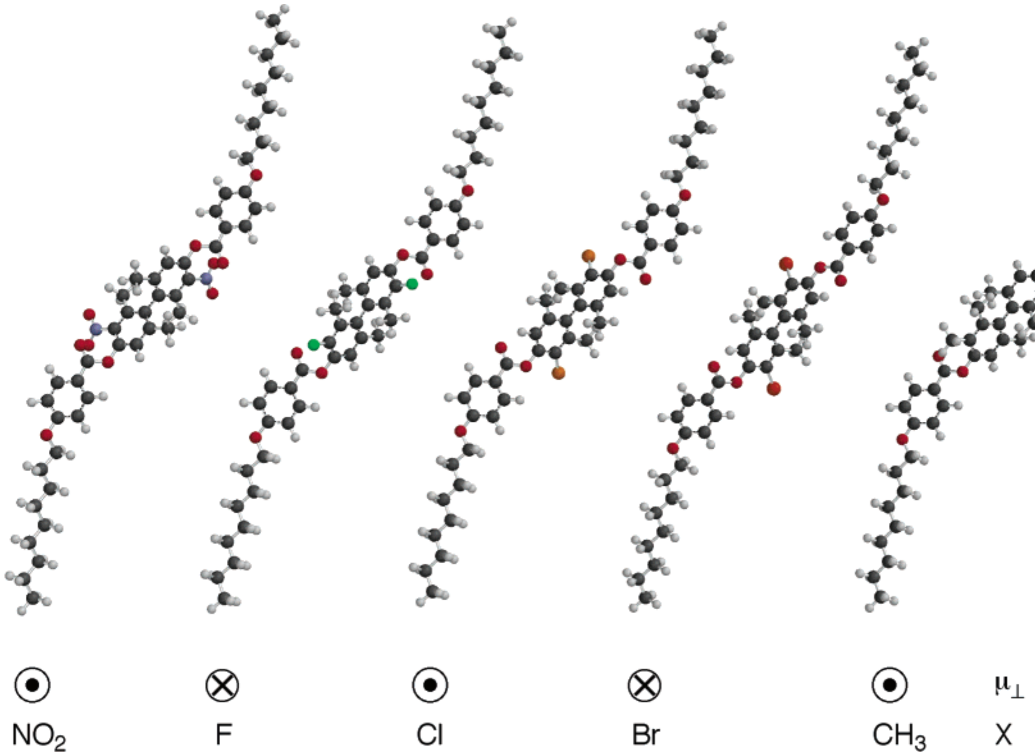


Figure 5. AM1-minimized structures for dopants (*R*)-**1** and (*S*)-**2**−**5** as side-on views with the dihedral angle ϕ formed by the C(O)−O bond and the plane of the phenyl ring fixed at the minimum energy value calculated at the B3LYP/6-31G(d) level. The transverse dipole moment vectors $\mu_\perp$ point from negative to positive according to the physics convention.

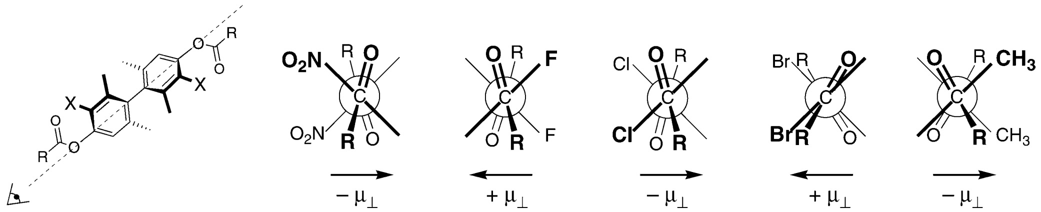


Figure 6. Schematic end-on views of the AM1-minimized structures from Figure 5 as Newman projections along the central C−C bond of the biphenyl core. The polar axis of the SmC* phase is oriented horizontally in the plane of the page.

concept of chirality transfer feedback, which extends the application of the Boulder model to dopants with axially chiral cores.

Experimental Section

General. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC-200 and Avance 300, 400, and 500 spectrometers in deuterated chloroform; chemical shifts are reported in δ (ppm) relative to tetramethylsilane. Low-resolution EI mass spectra were recorded on a Fisons VG Quattro triple quadrupole mass spectrometer; peaks are reported as *m/z* (% intensity relative to the base peak). High-resolution EI and ESI mass spectral analyses were performed by the University of Toronto mass spectrometry service. Melting points were measured on a Fisher-Johns melting point apparatus and are uncorrected. Conformational analyses and transverse dipole moment calculations were performed at the AM1 level using Spartan 02 (Wavefunction, Inc., Irvine, CA).

Materials. All reagents, chemicals, and liquid crystal hosts were obtained from commercial sources and used without further purification unless otherwise noted. Tetrahydrofuran (THF) was distilled from sodium/benzophenone under argon. 4-Bromo-3,5-dimethylanisole (**6**) was synthesized according to a literature procedure and shown to have the expected physical and spectral properties.[16] The five dopants (*R*)-**1** and (*S*)-**2**−**5** were obtained by reaction of the corresponding dihydroxybiphenyls (*R*)-**11** and (*S*)-**13**-**16** with 4-nonyloxybenzoic acid in the presence of DCC and DMAP according to the literature procedure and were shown to have the expected physical and spectral properties.[15,20]

4,4′-Dimethoxy-2,2′,6,6′-tetramethylbiphenyl (7). Under an argon atmosphere, a 1.56 M solution of *n*-BuLi in hexanes (59.5 mL, 93 mmol) was added dropwise to a solution of **6** (19.8 g, 92 mmol) in dry THF (500 mL) cooled to −78 °C. After stirring for 20 min, the solution was treated with solid CuCN (4.14 g, 46 mmol) and stirred for 2.5 h. The resulting cloudy mixture was removed from the cooling bath until it became clear, cooled back to −78 °C, and oxygen was bubbled in the solution for 3 h via a CO_2(s)/IPA trap. The oxygen flow was discontinued and the reaction mixture was allowed to warm to room-temperature overnight. After treatment with a 20% solution of NH_4OH in sat aq NH_4Cl (250 mL), the organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were washed with 20% NH_4OH in sat aq NH_4Cl, water (2×), and brine, dried (Na_2SO_4), and concentrated to a brown oil. Purification by flash chromatography (7:3 toluene/hexanes, then with 95:5 hexanes/EtOAc) gave 6.29 g (50%) of **7** as a white solid: mp 75−78 °C. ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.87 (s, 12H), 3.82 (s, 6H), 6.67 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 55.3, 113.0, 132.5, 137.7, 158.5. MS (EI) *m/z* 270 (M^+, 100), 255 (45), 240 (38), 225 (18), 209 (13), 197 (14), 181 (15), 165 (26), 128 (30), 120 (28). HRMS (EI) calcd for $C_{18}H_{22}O_2$: 270.1620. Found: 270.1617.

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[20] Vizitiu, D.; Lazar, C.; Halden, B. J.; Lemieux, R. P. *J. Am. Chem. Soc.* **1999**, *121*, 8229.

(*RS*)-4,4′-Dimethoxy-2,2′,6,6′-tetramethyl-3,3′-dinitrobiphenyl (8). To a stirred solution of **7** (4.90 g, 18.1 mmol) in glacial acetic acid (100 mL) was added dropwise concentrated HNO_3 (55 mL). The reaction mixture was stirred for 10 min at room temperature, then treated with concentrated H_2SO_4 (12 mL) and stirred for 2 h. The mixture was poured into water (200 mL) and the resulting precipitate was isolated by filtration, washed with water, and dissolved in EtOAc. The solution was washed with water, sat aq $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated to give 6.29 g (96%) of **8** as an orange solid: mp 211−212 °C. ^1H NMR (200 MHz, $CDCl_3$) δ 1.84 (s, 6H), 1.94 (s, 6H), 3.91 (s, 6H), 6.83 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 20.6, 56.2, 111.7, 129.2, 130.6, 139.8, 140.9, 149.8. MS (EI) *m/z* 360 (M^+, 57), 343 (55), 288 (7), 254 (29), 223 (34), 208 (25), 194 (38), 178 (52), 165 (100), 152 (71), 141 (45), 128 (80), 115 (57). HRMS (EI) calcd for $C_{18}H_{20}N_2O_6$: 360.1321. Found: 360.1322.

(*RS*)-3,3′-Diamino-4,4′-dimethoxy-2,2′,6,6′-tetramethylbiphenyl (9). A stirred mixture of **8** (3.85 g, 10.7 mmol) and $SnCl_2{\cdot}2H_2O$ (29.1 g, 129 mmol) in abs EtOH (250 mL) was refluxed overnight. After cooling, it was poured into water (200 mL) and diluted with 20% aq NaOH until basic. The cloudy mixture was extracted with EtOAc (2×) and the combined extracts were washed with water (2×) and brine, dried (Na_2SO_4), and concentrated to a white solid. Purification by flash chromatography on silica gel (1:1 hexanes/EtOAc) gave 2.54 g (79%) of **9** as a white solid: mp 160−162 °C. ^1H NMR (200 MHz, $CDCl_3$) δ 1.73 (s, 6H), 1.81 (s, 6H), 3.66 (br s, 4H), 3.88 (s, 6H), 6.61 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.6, 19.8, 55.4, 109.4, 121.4, 125.4, 131.7, 132.9, 145.8. MS (EI) *m/z* 300 (M^+, 100), 285 (54). HRMS (EI) calcd for $C_{18}H_{24}N_2O_2$: 300.1838. Found: 300.1851.

(*R*)- and (*S*)-3,3′-bis[(1*S*)-10-camphorsulfonamido]-2,2′,6,6′-tetramethyl-4,4′-dimethoxybiphenyl ((*S,S,R*)-10 and (*S,S,S*)-10). A solution of (1*S*)-(+)-10-camphorsulfonyl chloride (5.17 g, 20.6 mmol) in CH_2Cl_2 (20 mL) was added dropwise to a stirred solution of **9** (2.89 g, 9.62 mmol) and Et_3N (6.7 mL, 48 mmol) in CH_2Cl_2 (50 mL). The mixture was stirred at room temperature for 2 h, then diluted with EtOAc and washed with 5% aq HCl (2×), water, sat aq $NaHCO_3$, and brine, dried ($MgSO_4$), and concentrated to a white solid. Purification by flash chromatography on silica gel (3:2 EtOAc/hexanes) gave 6.83 g (97%) of a 1:1 mixture of (*S,S,R*)-**10** and (*S,S,S*)-**10**. The diastereomers were resolved by repeated, alternating recrystallizations from toluene and MeOH to give (*S,S,S*)-**10** (2.88 g, 42%) and (*S,S,R*)-**10** (2.56 g, 36%), respectively. Data for (*S,S,S*)-**10**: mp 210−222 °C. $[\alpha]_D$ +44° (*c* 0.21, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.96 (s, 6H), 1.01 (s, 6H), 1.45 (m, 2H), 1.90 (s, 6H), 1.99 (s, 6H), 2.00−2.20 (m, 10H), 2.45 (m, 2H), 3.02 (d, $J = 14.9$ Hz, 2H), 3.76 (d, $J = 14.9$ Hz, 2H), 3.83 (s, 6H), 6.70 (s, 2H), 7.43 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.7, 19.8, 20.2, 20.5, 27.2, 27.4, 43.1, 43.1, 48.6, 52.4, 55.7, 59.89, 110.3, 122.4, 133.5, 136.5, 138.4, 153.3, 216.3. MS (EI) *m/z* 728 (M^+, 2), 449 (26), 298 (41), 283 (38), 123 (32), 109 (72), 81 (100). HRMS (ESI) calcd for $C_{38}H_{53}N_2O_8S_2$ ($M+H^+$): 729.3237. Found: 729.3212. Data for (*S,S,R*)-**10**: mp 165−170 °C. $[\alpha]_D$ +46° (*c* 0.24, $CHCl_3$). ^1H NMR ($CDCl_3$, 500 MHz) δ 0.94 (s, 6H), 1.04 (s, 6H), 1.42 (m, 2H), 1.88 (s, 6H), 1.90−2.10 (m, 12H), 2.11 (t, $J = 4.4$ Hz, 2H), 2.26 (m, 2H), 2.42 (m, 2H), 3.04 (d, $J = 14.7$ Hz, 2H), 3.72 (d, $J = 15.0$ Hz, 2H), 3.85 (s, 6H), 6.70 (s, 2H), 7.14 (s, 2H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 16.6, 19.9, 20.1, 20.5, 26.91, 27.1, 43.0, 43.0, 48.5, 51.5, 55.6, 59.6, 110.1, 122.3, 133.5, 136.2, 138.4, 153.2, 216.2. MS (EI) *m/z* 728 (M^+, 2), 664 (8), 514 (13), 449 (52), 298 (56), 283 (65), 269 (33), 253 (26), 239 (20), 224 (15), 123 (35), 109 (92), 81 (100). HRMS (EI) calcd for $C_{38}H_{52}N_2O_8S_2$: 728.3165. Found: 728.3167.

X-ray Crystallography. Data collection was performed on a crystal of (*S,S,R*)-**10**$\cdot CH_3OH$ (colorless, plate-shaped, size 0.40 × 0.38 × 0.30 mm) using a Bruker SMART CCD 1000 X-ray diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) operating at 50 kV and 35 mA at 25 °C over 2θ ranges of 3.06 to 56.56°. Data were processed using the Bruker AXS Windows NT SHELLXTL software package (version 5.10).[21] Neutral atom scattering factors were taken from Cromer and Waber.[22] The raw intensity data were converted (including corrections for scan speed, background, and Lorentz and polarization effects) to structure amplitudes and their esd's using the program SAINT, which corrects for *L*p and decay. The absorption corrections were applied using the program SADABS. The crystal is orthorhombic space group $P2_1$, based on the systematic absences, *E* statistics, and successful refinement of the structure. The structure was solved by direct methods. Full-matrix least-squares refinements minimizing the function $\Sigma w(F_o^2 - F_c^2)^2$ were applied to the compound. All non-hydrogen atoms were refined anisotropically although one of the camphor groups is disordered. The positions for all hydrogen atoms were calculated, and their contributions were included in the structure factor calculations with isotropic thermal parameters 1.2 times that of the attached carbon atoms (1.5 times for methyl hydrogens). Convergence to final $R_1 = 0.0466$ and $wR_2 = 0.1129$ using 7765 independent reflections and 514 parameters was achieved,[23] with the largest residual peak and hole as 0.228 and −0.212 e/Å^3, respectively.

(*R*)-4,4′-Dimethoxy-2,2′,6,6′-tetramethyl-3,3′-dinitrobiphenyl ((*R*)-8). To a stirred mixture of (*S,S,R*)-**10** (1.86 g, 2.55 mmol) in glacial AcOH (25 mL) was added concentrated HBr (2.5 mL). The mixture was refluxed for 3 h, then cooled, poured into water (200 mL), and treated with 20% aq NaOH until basic (pH = 9). The resulting precipitate was isolated by filtration, washed with water, and dissolved in EtOAc. The solution was washed with water and brine, dried ($MgSO_4$), and concentrated, and the crude product was purified by flash chromatography on silica gel (6:4 hexanes/EtOAc) to give 0.59 g (72%) of (*R*)-**9** as a yellowish solid. The product was dissolved in $CHCl_3$ (50 mL), cooled to 0 °C, and a solution of mCPBA (4.3 g, ~75% purity, 19 mmol) in $CHCl_3$ (70 mL) was added dropwise. The mixture was stirred at 0 °C for 48 h, then warmed to room temperature and treated with sat aq $NaHCO_3$. The organic layer was separated, washed with 2% aq NaOH (2×), water, and brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (7:3 hexanes/EtOAc) gave 162 mg (24%) of (*R*)-**8** as a yellow oil with spectral properties identical to those of racemic **8**: $[\alpha]_D$ +5° (*c* 1.3, $CHCl_3$).

(*R*)-4,4′-Dihydroxy-2,2′,6,6′-tetramethyl-3,3′-dinitrobiphenyl ((*R*)-11). Under a N_2 atmosphere, a 1.0 M solution of BBr_3 in heptane (2.5 mL, 2.5 mmol) was added dropwise to a stirred solution of (*R*)-**8** (162 mg, 0.45 mmol) in CH_2Cl_2 (5 mL) cooled to −78 °C. The reaction mixture was allowed to warm slowly to room-temperature overnight, then poured into water and stirred for 1 h. The mixture was extracted with EtOAc and the organic layer was washed with water (2×) and brine, dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel ($CHCl_3$) gave 100 mg (67%) of (*R*)-**11** as a yellow solid which showed the expected physical and spectral properties.[20]

(*S*)-3,3′-Diamino-4,4′-dimethoxy-2,2′,6,6′-tetramethylbiphenyl ((*S*)-9). The procedure used for the hydrolysis of (*S,S,R*)-**10** was repeated with (*S,S,S*)-**10** (2.84 g, 3.90 mmol) to give 466 mg (40%) of (*S*)-**9** as a white solid with spectral properties identical to those of racemic **9**: mp 174−176 °C. $[\alpha]_D$ +3° (*c* 0.7, $CHCl_3$).

(*S*)-3,3′-Diiodo-4,4′-dimethoxy-2,2′,6,6′-tetramethylbiphenyl ((*S*)-12). A solution of $NaNO_2$ (200 mg, 2.90 mmol) in water (5 mL) was added dropwise to a stirred solution of (*S*)-**9** (413 mg, 1.38 mmol) in 10% aq H_2SO_4 (10 mL) cooled in an ice bath. The reaction mixture was stirred at 0 °C for 30 min, then added dropwise to a stirred, ice-cold solution of KI (1.18 g, 7.1 mmol) in water (10 mL). The mixture was refluxed for

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(21) SHELXTL NT: Crystal Structure Analysis Package, version 5.10; Bruker AXS Inc.: Madison, WI, 1999.

(22) Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, UK, 1974; Vol. 4, Table 2.2 A.

(23) $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ ($w = 1/[\sigma^2(F_o^2) + (0.0709P)^2]$, where $P = [\mathrm{Max}(F_o^2, 0) + 2F_c^2]/3$).

2 h, then diluted with EtOAc and water. The organic layer was washed with 10% aq HCl, sat aq $NaHCO_3$ and aq $Na_2S_2O_3$, dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (1:1 hexanes/toluene) followed by recrystallization from hexanes gave 382 mg (53%) of (*S*)-**12** as a white solid: mp 162−168 °C. $[\alpha]_D$ +39° (*c* 0.76, $CHCl_3$). ^1H NMR ($CDCl_3$, 400 MHz) δ 1.85 (s, 6H), 2.08 (s, 6H), 3.91 (s, 6H), 6.62 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5, 26.2, 56.5, 90.9, 110.3, 133.8, 137.3, 140.8, 157.0. MS (EI) *m/z* 522 (M^+, 6), 253 (15), 238 (11), 223 (16), 210 (16), 195 (24), 178 (38), 165 (100), 152 (62), 128 (56). HRMS (EI) calcd for $C_{18}H_{20}I_2O_2$: 521.9553. Found: 521.9561.

(*S*)-3,3′-Dichloro-4,4′-dihydroxy-2,2′,6,6′-tetramethylbiphenyl ((*S*)-13). A mixture of (*S*)-**12** (33 mg, 0.0625 mmol) and CuCl (138 mg, 1.39 mmol) in dry DMF (1.5 mL) was refluxed overnight under argon. After cooling, the reaction mixture was poured into concentrated NH_4OH and extracted with Et_2O. The organic layer was washed with water (2×), dried ($MgSO_4$), and concentrated. The crude product was then dissolved in CH_2Cl_2 (2 mL), cooled to −78 °C under argon, and treated with a 1.0 M solution of BBr_3 in hexanes (0.25 mL, 0.25 mmol). The reaction mixture was allowed to warm slowly to room-temperature overnight, then poured into water and stirred for 1 h. The mixture was extracted with EtOAc and the organic layer was washed with water (2×), dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel ($CHCl_3$) gave 14.5 mg (68%) of (*S*)-**13** as a colorless film which showed the expected physical and spectral properties.[20]

(*S*)-3,3′-Dibromo-4,4′-dihydroxy-2,2′,6,6′-tetramethylbiphenyl ((*S*)-14). A mixture of (*S*)-**12** (32.4 mg, 0.062 mmol) and CuBr (217 mg, 1.51 mmol) in pyridine (1.5 mL) was refluxed overnight under argon. Afer cooling, the reaction mixture was poured into concentrated NH_4OH and extracted with EtOAc. The organic layer was washed with water, 10% aq HCl, and water (2×), dried ($MgSO_4$), and concentrated. After elution through a silica gel plug (toluene), the product was dissolved in CH_2Cl_2 (2 mL), cooled to −78 °C under argon, and treated with a 1.0 M solution of BBr_3 in hexanes (0.25 mL, 0.25 mmol). The reaction mixture was allowed to warm slowly to room-temperature overnight, then poured into water and stirred for 3 h. The mixture was extracted with EtOAc and washed with water (2×), dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel ($CHCl_3$) gave 17.2 mg (70%) of (*S*)-**14** as a colorless film which showed the expected physical and spectral properties.[20]

(*S*)-3,3′-Difluoro-4,4′-dihydroxy-2,2′6,6′-tetramethylbiphenyl ((*S*)-15). Under an argon atmosphere, a 1.6 M solution of *n*-BuLi in hexanes (0.10 mL, 0.16 mmol) was added dropwise to a stirred solution of (*S*)-**12** (31 mg, 0.06 mmol) in dry THF (1.5 mL) cooled to −78 °C. After stirring for 10 min, a solution of $(PhSO_2)_2NF$ (116 mg, 0.368 mmol) in dry THF (1.5 mL) was added dropwise and the solution was allowed to warm slowly to room-temperature overnight. The reaction was quenched with sat aq NH_4Cl and partitioned between EtOAc and aq K_2CO_3. The organic layer was washed with aq K_2CO_3, dried ($MgSO_4$), and concentrated. After purification by flash chromatography on silica gel (9:1 hexanes/EtOAc), the product was dissolved in CH_2Cl_2 (1.5 mL), cooled to −78 °C under argon and treated with a 1.0 M solution of BBr_3 in hexanes (0.25 mL, 0.25 mmol). The reaction mixture was allowed to warm to room-temperature overnight, then poured into water and stirred for 15 min. The mixture was extracted with EtOAc, and the organic layer was washed with water (2×), dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (7:3 hexanes/EtOAc) gave 10.6 mg (63%) of (*S*)-**15** as a colorless film which showed the expected physical and spectral properties.[20]

(*S*)-4,4′-Dihydroxy-2,2′,3,3′,6,6′-hexamethylbiphenyl ((*S*)-16). Under an argon atmosphere, a 1.6 M solution of *n*-BuLi in hexanes (0.10 mL, 0.16 mmol) was added dropwise to a stirred solution of (*S*)-**12** (32.8 mg, 0.0623 mmol) in dry THF (1.5 mL) cooled to −78 °C. After stirring for 2 min, a 2.0 M solution of MeI in *tert*-butyl methyl ether (0.16 mL, 0.32 mmol) was added dropwise and the reaction mixture was allowed to warm to room-temperature overnight. The reaction mixture was quenched with saturated aqueous NH_4Cl and partitioned between water and EtOAc. The organic layer was separated and washed with water (2×), dried ($MgSO_4$), and concentrated. The crude product was dissolved in CH_2Cl_2 (2 mL), cooled to −78 °C under argon, and treated with a 1.0 M solution of BBr_3 in hexanes (0.25 mL, 0.25 mmol). The reaction mixture was allowed to warm slowly to room-temperature overnight, then poured into water and stirred for 20 min. The mixture was extracted with EtOAc, and the organic layer washed with water (2×), dried ($MgSO_4$), and concentrated. Purification by flash chromatography on silica gel (4:1 hexanes/EtOAc) gave 10.6 mg (63%) of (*S*)-**16**, contaminated with ca. 10% of the achiral monoreduced product, which showed the expected physical and spectral properties.[20]

Ferroelectric Polarization Measurements. Texture analyses and transition temperature measurements for the doped liquid crystal mixtures were performed using a Nikon Labophot-2 POL polarized microscope fitted with a Linkam LTS 350 hot stage. Polyimide-coated ITO glass cells (4 μm × 0.160 cm^2) supplied by E. H. C. Co. were used for each measurement. Good alignment was obtained by slow cooling of the filled cells from the isotropic phase via the N* and SmA* phases. The sign of P_S was determined at 5 K below the SmC*−SmA* transition temperature ($T - T_C = -5$ K) from the relative configuration of the electric field and the switching position of the sample according to the established convention.[6]

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Supporting Information Available: X-ray crystallographic data for (*S*,*S*,*R*)-**10** including structure refinement parameters and tables of atomic coordinates, anisotropic thermal parameters, bond lengths and bond angles in CIF file format. The material is available free of charge via the Internet at http://pubs.acs.org.

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